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Ion Exchange Membrane Methods for Continuous Removal of Ions from Water and Trace Chemical Analysis

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F I N A L R E P O R T

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PUBLICATIONS AND PRESENTATIONS OF RESULTS OF THE STUDY

1. J. A. Cox and J. E. DiNunzio, "Donnan Dialysis of Cations," Anal. Chem. 49 1272 (1977).

2. J. E. DiNunzio, "Donnan Dialysis for the Enrichment of Cations," Ph.D. Dissertation, SIU-C, 1977.

3. J. A. Cox and K. H. Cheng, "Donnan Dialysis of Anions of Weak Acids," Anal. Chem 50 601 (1978).

4. J. A. Cox and K. H. Cheng, "Donnan Dialysis Matrix Normalization for Cathodic Stripping Voltammetry," Anal. Lett. A11 653 (1978).

5. K. H. Cheng, "Cathodic Stripping Methods for the Determination of Phosphate and Arsenate," Ph.D. Dissertation, SIU-C, 1977.

6. J. A. Cox and G. Litwinski, "Design of a Voltammetric Ion Selective Electrode," in preparation.

7. J. A. Cox and M. Majda, "Anodic Behavior of Lead Electrodes in Phosphate Medium," in preparation.

8. J. A. Cox, "Donnan Dialysis Matrix Normalization for Electroanalytical Methods," Joint Great Lakes/Central Regional American Chemical Society Meeting, May, 1978.

9. J. A. Cox and M. Majda, "Formation of Phosphate Films on Lead Electrodes," Joint Great Lakes/Central Regional American Chemical Society Meeting, May, 1978.

10. J. A. Cox and A. Brajter, "Mechanism of the Zr(IV) Catalyzed Reduction of Nitrate," Joint Great Lakes/ Central Regional American Chemical Society Meeting, May, 1978.

11. J. A. Cox and J. E. DiNunzio, "Donnan Dialysis Pretreatment for Atomic Absorption Spectrometry," Great Lakes Regional American Chemical Society Meeting, June, 1977.

12. J. A. Cox, "Design of a Voltammetric Ion Selective Electrode for Nitrate," Midwest Universities Analytical Chemistry Conference, Oct., 1978.

1. Introduction and Objectives

Ion exchange membranes are utilized primarily in the technique of electrodialysis, a method which is widely used to remove salts from samples. The need for a large power supply, the tendency to incur membrane fouling, and the lack of a means of transferring a given ionic species across the membrane independent of the other components in a sample are limitations on electrodialysis.

Donnan dialysis has been shown to be an effective means of transferring ionic species from a sample into a receiver electrolyte (1-3). In this method the ion exchange membrane is placed between the sample solution and the relatively high ionic strength receiver electrolyte. Donnan exclusion acts to hinder transfer of co-ions (those of the same charge sign as the fixed exchange sites on the membrane) across the membrane but permits counter-ion flux. The concentration difference between the sample and receiver favors transfer of counter-ions from the latter to the former; but because electrostatic equilibrium must be maintained, the extent of this transfer is limited by the availability of counter-ions in the sample which can enter the receiver.

By this mechanism, transfer of certain ionic species was shown to be directly proportional to the original

sample concentration, independent of sample ionic strength up to the 0.01 level, independent of the sample volume as long as it was at least 10-times greater than the receiver volume, independent of time as long as Donnan equilibrium is not approached (i.e., less than 2 hr for typical conditions), and insensitive to stirring rate (1,4). In addition, membrane fouling by surfactants was not observed (1,4). Thus, Donnan dialysis was shown to possess certain advantages over electrodialysis.

Based upon the above observations, a detailed evaluation and preliminary application of Donnan dialysis was initiated. The primary objectives were (A) to determine whether Donnan dialysis coupled to electrochemical deposition could be used as a means of continuously removing selected ions from water and (B) to test whether Donnan dialysis could be used to improve certain analytical methods when used on various water and wastewater samples. Prior to addressing these objectives it was necessary to further study the problem of Donnan dialysis so that transfer conditions could be optimized in terms of rate and independence of the sample matrix.

2. Donnan Dialysis of Cations

Factors which influence the rate of Donnan dialysis of cations have not previously been systematically investigated. As the mechanism of the transfer has generally been assumed to be diffusion-controlled, previous studies have typically used receiver electrolytes which contained highly mobile counter-ions, eg., Na^+, Li^+, and H^+. In the present study it was demonstrated that high charge density counter-ions yielded greater transfer rates as well as values which are independent of the sample composition.

Experimental

The cation exchange membranes were type P-1010 and P-4010 (RAI Research Corporation, Hauppauge, Long Island, New York) and Nafion 125 (DuPont). They were pretreated by the procedure of Blaedel and Kissel (5) except that the Nafion 125 was boiled for 30 min in H_2O prior to pretreatment and not cycled in acid and base. The membranes were mounted on the 2-cm diameter base of glass cylinders and attached with Teflon tape and o-rings. The completed cells were soaked in 1-2 M receiver electrolyte for 30 min and stored in contact with electrolyte at the concentration to be used in the experiment.

In the procedure from 2-6 mL of electrolyte was pipetted into the cell. The transfer was initiated by placing the membrane face of the cell in contact with a magnetically-stirred 200 mL sample; the receiver electrolyte remained unstirred. After a prescribed time the cell was removed; and the inner solution was quantitatively transferred to a volumetric flask, diluted to volume, and poured into a plastic storage bottle. All analyses were subsequently performed within 24 hr.

The solvent extraction experiments which were performed for comparison utilized a procedure reported elsewhere (6,7). The copper extraction employed ammonium pyrrolidine dithiocarbamate (APDC) as the complexing agent and methyl isobutyl ketone (MIBK) as the solvent. Comparative columnar ion exchange studies used a previously reported procedure (8); the column contained 5.4 gm of Amberlite IR-120 and was operated at a 3-4 mL/min flow rate.

The primary apparatus which was used was a Jarrell-Ash Model 82-528 Atomic Absorption Spectrophotometer. Certain determinations were repeated with a PAR Model 170 in the differential pulse polarography mode (Princeton Applied Research Corporation) in order to demonstrate that the observed phenomena were not associated with salt effects on the air-acetylene flame.

Temperature control was accomplished using a Forma Temp Jr Model 2095-2 bath and circulator in conjunction with a jacketed beaker. Controlled stirring was maintained by electronically monitoring the rotation frequency of the magnetic stirring motor and manually adjusting the unit when necessary.

Results and Discussion

Initial experiments were performed by transferring Cu(II) in the 10^{-4} M range into 0.1 M LiCl for 1 hr across at P-1010 membrane. The resulting Cu concentration in the receiver was not linearly related to the sample concentration; a positive deviation from linearity was observed. Based upon our previous experience with NO_3^- transfer across anion exchange membranes this deviation was unexpected. The same results were obtained with P-4010 and Nafion 125 membranes and with K^+ as the test ion rather than Cu(II); therefore, it was hypothesized that the increased sample ionic strength which occurs at the higher test ion concentrations accelerates the transfer rate.

Experiments summarized in Figure 1 verified the above hypothesis. In this case, various salts were added to an 8.8×10^{-6} M Cu(II) solution. Initially the added salt enhances the transfer, but above about

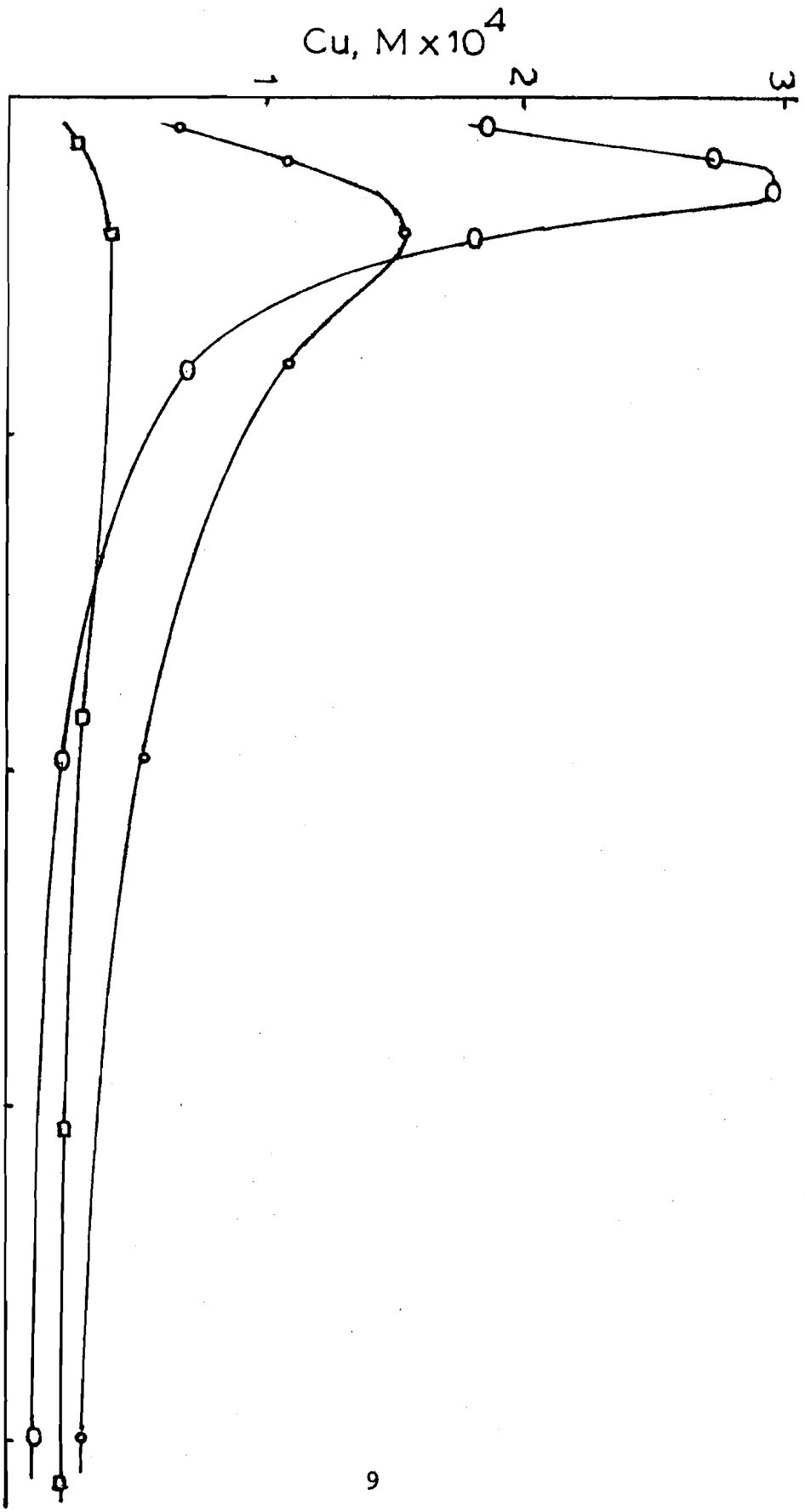

Figure 1. Effect of Various Counterions on the Transfer of Cu into 0.1 M LiCl. □ , K^+; O , Mg^{2+}; O, Al(III)

5×10^{-2}M the added salt decreases the enrichment rate because of a decrease in the Donnan potential when high ionic strength solutions are on each side of the membrane. In Table 1 are summarized data which demonstrate the effect of sample ionic strength.

Table 1

Effect of Sample Ionic Strength

on the Transfer of Cu into the Mg/Al Receiver

Added Salt	Ionic Strength	Relative Transfer (%)
4.0×10^{-5} M NaCl	.004	91
1.3×10^{-3} M $Fe(NO_3)_3$	.008	92
5.0×10^{-4} M $Al_2(SO_4)_3$	.008	86
1.0×10^{-3} M $Al_2(SO_4)_3$	.015	35
1.6×10^{-2} M NaCl	.016	43
6.0×10^{-2} M NaCl	.060	43
1.0×10^{-1} M NaCl	.100	35
1 M NaCl	1	0
---	---	100

Sample solution, 8.8×10^{-6} M $CuSO_4$; receiver electrolyte ionic strength 0.82 (0.2 M $MgSO_4$/5×10^{-4} M $Al_2(SO_4)_3$).

The results in Figure 1 indicate one means of normalizing the transfer of the test ion. An excess of Mg(II) was added to each Cu(II) sample prior to Donnan dialysis. Cd was also included to act as an internal standard. As shown in Figure 2, the transfer of the Cu(II) is linearized. The approach is not convenient, however, since Mg(II) and Cd(II) must be absent from the unknown sample; in addition, further experimentation demonstrated that Al(III) in the sample interfered by enhancing the Cu(II) transfer rate.

Examination of the results in Figure 1 and consideration of the fact that Al(III) interferes even when Mg(II) is present in excess suggest that the mechanism of the enhancement involves interaction with the fixed exchange sites on the membrane. Thus, a high charge density ion such as Al(III) can occupy these sites in preference to Cu(II), or displace the Cu(II) from these sites, and thereby increase the transfer rate. With this mechanism it should not matter whether the enhancing ion is added to the sample or used to replace the LiCl as the receiver electrolyte. Further, there should be a systematic trend of enrichment factor at a prescribed time with charge density of the receiver cation.

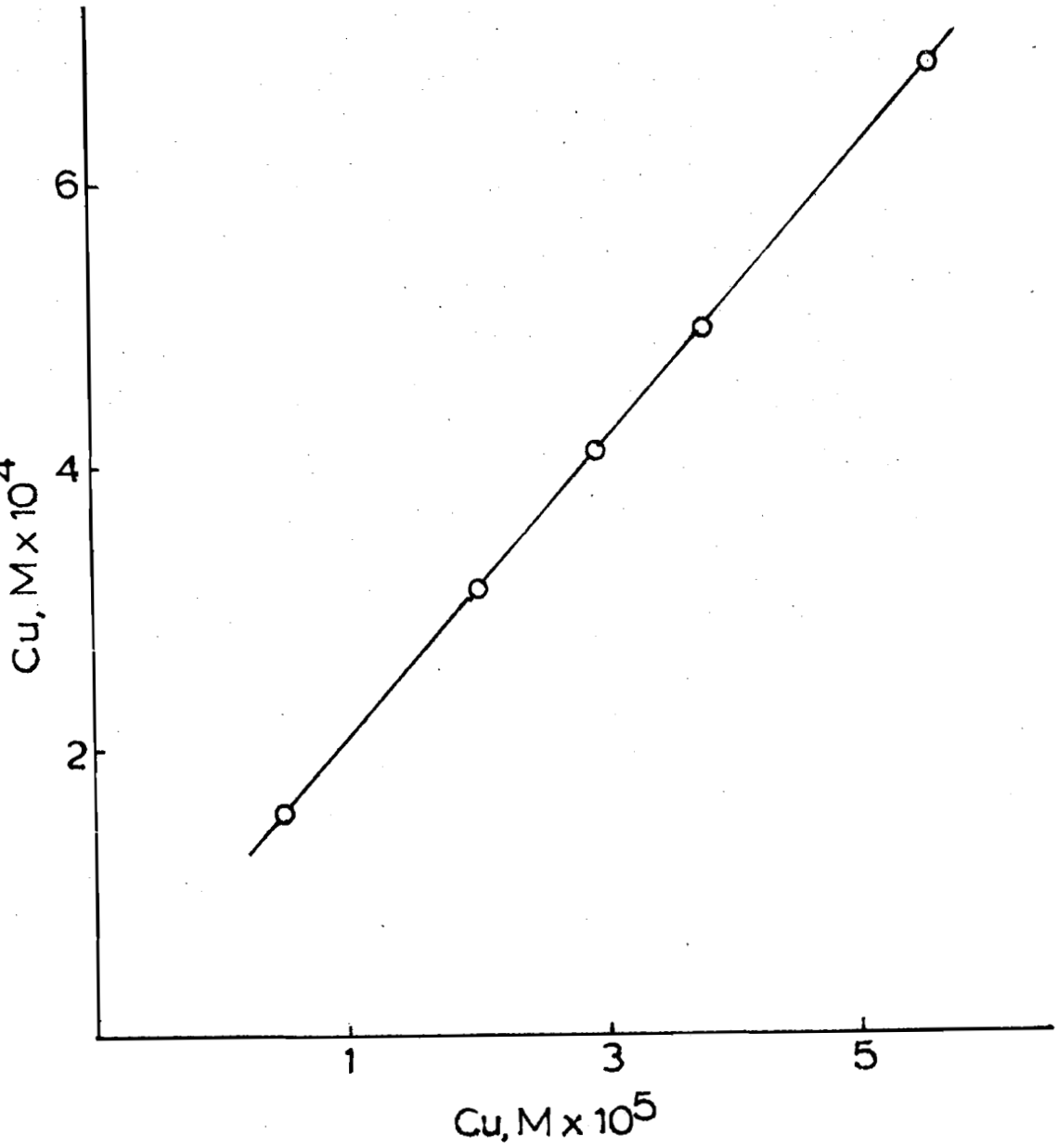

Figure 2. Atomic Absorption Working Curve for Cu after Donnan Dialysis. Receiver electrolyte, 5 mM Mg(II), 0.1 M LiCl; enrichment time, 1 hr.

Table 2 summarizes the results of a study in which the Cu(II) enrichment was measured as a function of the receiver counter-ion identity; in addition, the relative interference of counter-ions added to the sample was determined. It is evident that, considering Periodic Groups IA-IIIA, sample cations in a higher group number or of a lower atomic number within a given group, relative to the receiver cation, will interfere with the transfer. Hence, the optimum receiver should contain Al(III) as the counter-ion. Because of the limited solubility of Al-salts in neutral-to-slightly acidic aqueous solution, the receiver employed for most subsequent work was a 0.2 M $MgSO_4$, 5.0×10^{-4} M $Al_2(SO_4)_3$ mixture.

The use of a receiver electrolyte with an ionic strength of 0.8 was a result of the series of experiments which are summarized in Table 3. It is apparent that at higher ionic strengths, which would yield a higher Donnan potential, a greater transfer rate is produced. When the ionic strength is increased, dilution of the receiver electrolyte by osmosis also increases; 0.8 is a reasonable compromise value for ionic strength.

Table 2

Effect of a Counter-ion Added to the Sample on the Preconcentration of Cu into Various Receiver Electrolytes

Receiver Electrolyte	Added Counter-ion, x 10^3 M	Enrichment Factor	Cu/Co
0.2 M $MgSO_4$	---	7.0	.72
	H^+, 0.001	7.0	.72
	H^+, 1.0	7.2	.71
	Ca(II), 0.2	6.8	.74
	Ca(II), 0.6	7.0	.70
	Ca(II), 1.0	7.1	.69
	Al(III), 0.06	10.1	.38
	Al(III), 0.5	12.0	.25
	Al(III), 2.0	5.1	.39
0.3 M $CaCl_2$	---	5.2	.68
	Mg(II), 0.2	5.2	.70
	Mg(II), 0.6	5.2	.68
	Mg(II), 1.0	5.2	.70
0.3 M $BaCl_2$	---	4.0	.73
	Mg(II), 0.2	4.6	.78
	Mg(II), 0.6	2.6	.87
	Mg(II), 1.0	2.1	.66
Mg/Al*	---	10.4	.59
	Al(III), 0.04	10.3	.59
	Al(III), 0.1	10.4	.60
	Al(III), 0.8	10.4	.57
	Al(III), 1.0	10.3	.58
	Fe(III), 0.07	9.4	.61
	Fe(III), 0.4	9.6	.61
	Fe(III), 1.0	9.6	.61

Sample Solution, 8.8x 10^{-6} M $CuSO_4$

* 0.2 M $MgSO_4$/5x10^{-4} M $Al_2(SO_4)_3$

Table 3

Effect of Receiver Ionic Strength on the Enrichment of Cu Samples

Receiver	Ionic strength	Enrichment factor*
0.1 M LiCl	0.1	0.80
0.2 M LiCl	0.2	2.7
0.3 M LiCl	0.3	4.3
0.1 M Li_2SO_4	0.3	4.5
0.2 M Li_2SO_4	0.6	8.3
0.3 M Li_2SO_4	0.9	9.4

*Receiver Cu concentration after 1 h divided by the original sample concentration, 8.8×10^{-6} M; the former concentration is corrected for dilution by osmosis in the high ionic strength samples.

The dilution of the receiver electrolyte by osmosis is still significant at the recommended ionic strength. For example, in 1 hr the 4.0 mL Mg, Al mixture is diluted to 4.6 mL. Thus, to eliminate quantitative error in the eventual analysis one must either dilute the final receiver to a known volume, which will decrease the enrichment capabilities of Donnan dialysis, or use an internal standard, which is somewhat inconvenient. Even with the latter approach,

the enrichment factor is decreased.

The use of a complexing agent in the receiver electrolyte was found to yield a high enrichment factor without the requirement of a high ionic strength. For example, a receiver consisting on 10^{-4}M EDTA, 0.1 M LiCl at pH 4.5 enriches Cu(II) by the same factor as into the 0.2 M $MgSO_4$, 5 x 10^{-4}M Al(III) receiver. Similar results were observed when Zn and Pb were the test ions.

The above results cast doubt on the widely accepted theory that Donnan dialysis is a diffusion controlled process. Instead it would appear that under the conditions in which the receiver is a simple salt solution such as LiCl or NaCl the rate of Donnan dialysis is determined by the strength of the interaction between the test species and the fixed exchange sites. The use of a high charge density counter-ion in the receiver, or a strong complexing agent, favors the release of the test ion; under such conditions the transfer may now approach diffusion control. An important analytical aspect of the effect of complexing agents is that Donnan dialysis may be capable of performing selective enrichment of certain metals.

Even when an internal standard is not needed to correct for dilution by osmosis, it can be needed in a Donnan dialysis experiment in order to obtain high precision. The primary factors which govern the

precision of a Donnan dialysis preconcentration are temperature, membrane area, and stirring rate. The transfer rate across the membrane is directly proportional to temperature over the range 20-50°C; it increases about 4% per degree in that range when 0.1 M KCl is the receiver electrolyte and Li is the test cation. Increasing the stirring rate from 4 to 7 Hz causes the transfer rate to double.

In the absence of an internal standard, the general effect of the above factors is to limit the precision of preconcentration to 8% relative standard deviation based upon a set of 8 identical experiments performed on different days at ambient temperature, 21-23°C, with nominal control of stirring. With a thermostated cell and controlled stirring, a 2% relative standard deviation is obtained; without a thermostated cell, but with a stirring control, it is 3%. These values refer to a series of experiments performed with the same cell so that variation in membrane area and thickness is not a factor.

If the above enrichment experiments are performed by using eight nominally identical cells in parallel with controlled temperature and stirring, the relative standard deviation increases to 6%, a value which illustrates the deviation of area and/or thickness of

the membranes. By inclusion of the internal standard, the precision is improved to 1.5% relative standard deviation if controlled temperature and stirring are employed and 2.1% if they are not. The fact that the use of the internal standard permits precise use of several cells in parallel without stringent control of temperature and stirring is important. Typical preconcentration times are from 0.5-2 h; therefore, if a batch determination had to be performed by repeated use of the same cell, the technique would not be practical.

In order to evaluate the relative merits of Donnan dialysis as an enrichment method for cations, a comparison to solvent extraction and columnar ion exchange was made. For reference a working curve was prepared by Donnan dialysis. For samples with ionic strengths lower than 0.01, a single working curve can be used. A working curve was obtained by preconcentrating samples in the range 1.4×10^{-7}-2.5×10^{-5} M Cu for 30 min into the Mg/Al receiver and subsequently determining the Cu concentration in the receiver electrolyte by atomic absorption with a 10-cm air-acetylene flame at 3247.5 Å. A linear least squares curve fit with a forced intercept at the origin yielded a slope (enrichment factor) of 9.44 with a standard

deviation of 3.8×10^{-6}. A 5.4×10^{-6}M Co(II) internal standard was used. The sample concentration of Cu which yielded 1% absorption at 3247.5 Å was 1.1×10^{-7} M (7 ppb Cu) under these conditions. The working curve utilized an internal standard in order to obtain high precision. The selection of Co(II) was based upon its having Donnan dialysis behavior similar to that of Cu(II). The similarity does not account for the linearity of the working curve, however (see Table 2).

A solvent extraction working curve was obtained. The results shown in Figure 3 demonstrate that the method becomes nonlinear at low concentrations in that the plot must curve to intercept the origin. Solvent extraction does have a lower limit of detectability, however. The Cu concentration which gives a 1% absorption is 3×10^{-8}M (2 ppb); to obtain the same sensitivity by Donnan dialysis would require a 2 hr enrichment.

A working curve prepared by columnar ion exchange is shown in Figure 4. In this case 200 mL of the listed Cu(II) concentration was exchanged on a column and subsequently eluted with 25 ml of 0.1 M HCl. The results are characterized by high data scatter; the standard deviation of a linear least squares curve fit is 18%. The method is also slow; about 3 hr of sample preparation time is needed per sample as compared to about 30 min for Donnan dialysis and 15 min for solvent

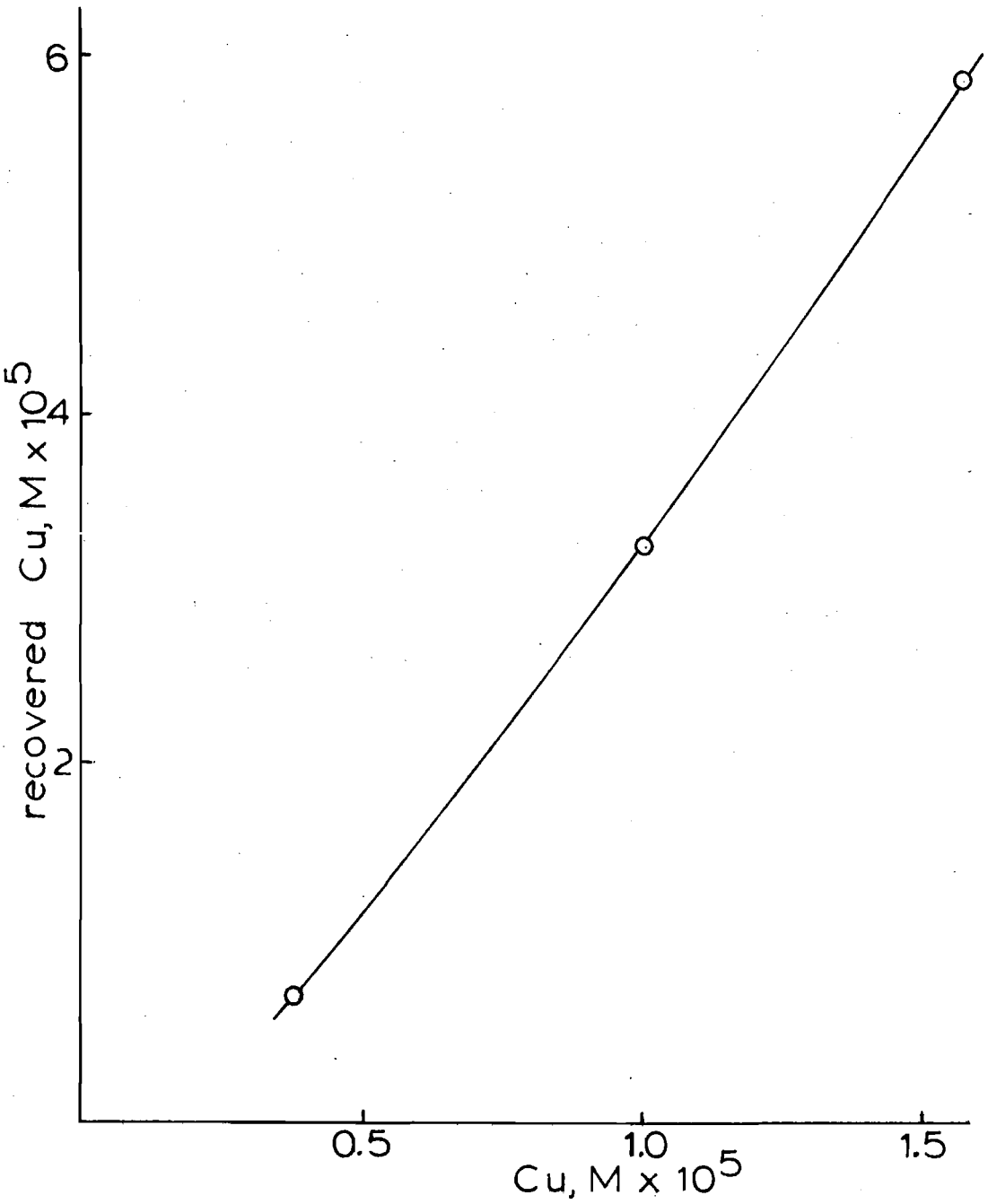

Figure 3. Atomic Absorption Working Curve for Cu after Solvent Extraction. Volume ratio, 5:1.

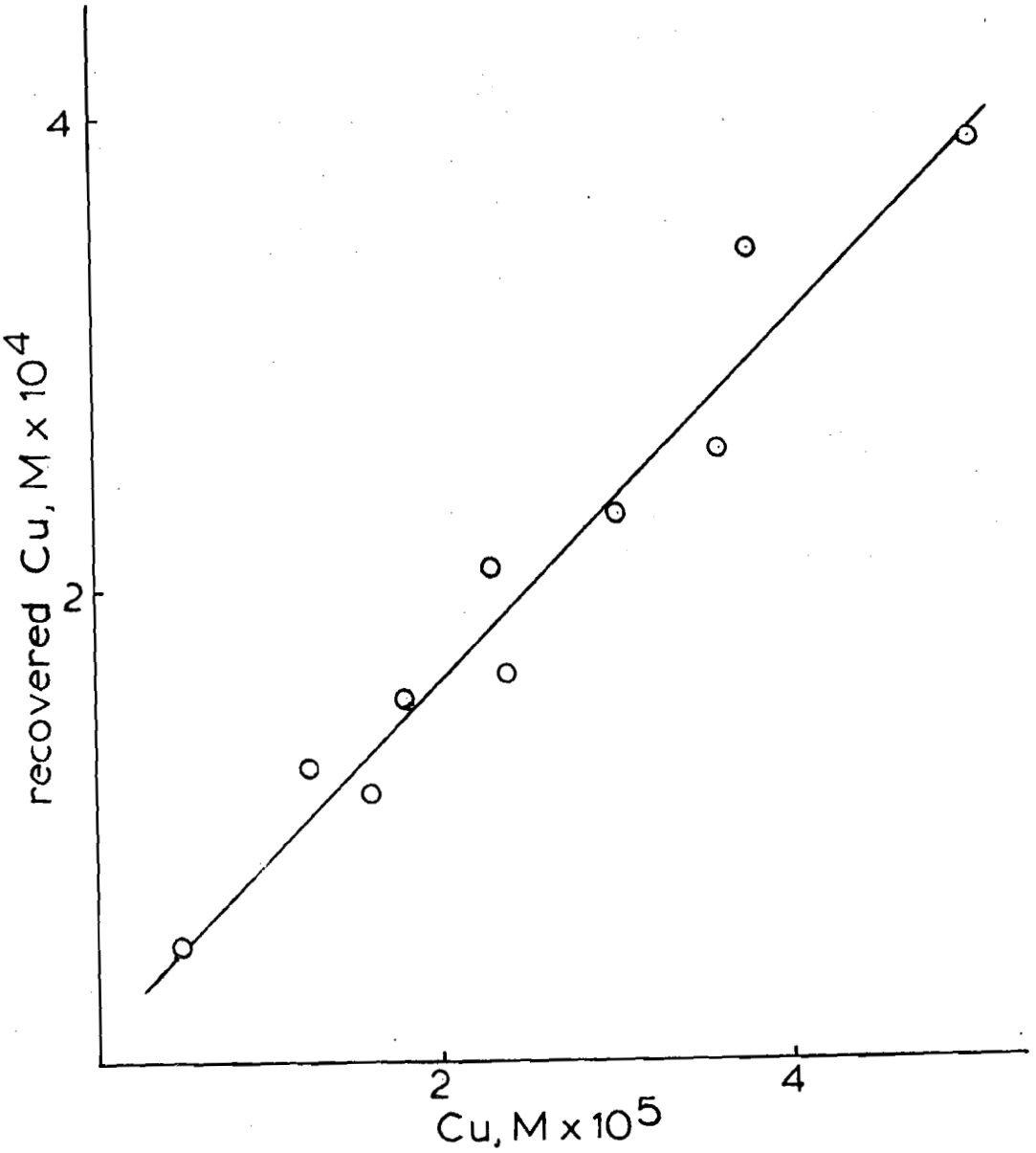

Figure 4. Atomic Absorption Working Curve for Cu after Columnar Ion Exchange.

extraction.

Conclusion

Donnan dialysis has been found to be a useful means of enriching cations. The method compares well with solvent extraction in that it can be used for a wider range of cations, has a greater linear dynamic range, and is probably less subject to interference. The latter point is illustrated by the fact that the enrichment of Cu into a 0.2 M Mg(II), 5 x 10^{-4} M Al (III) receiver occurs independently of the following components in samples as long as the sample ionic strength is less than 0.1: Periodic Group IA-IIIA metals, H^+, Cd, Co, Ni, Pb, Zn and Fe. The relative standard deviation of successive enrichments is 1.5% if an internal standard is used, 2-3% if the temperature and stirring rate are controlled, and 8% if no controls are used. We have recently reported these conclusions elsewhere (8), and a more detailed evaluation of certain aspects of Donnan dialysis of cations is also available (9).

3. Donnan Dialysis Enrichment of Anions of Weak Acids

Previously we had demonstrated that anions such as nitrate which are weak bases can be enriched by Donnan dialysis in a manner directly proportional to

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The analytical method which was used for the determination of phosphate and arsenate was the molybdenum blue spectrophotometric procedure (10). Sulfate was determined by the choranilate spectrophotometric method (11). Chloride, pyruvate, and chloroacetate were determined by pulse polarography or linear scan voltammetry.

The polarography and voltammetry experiments were performed with a PAR Model 170 Electrochemistry system, Princeton Applied Research Corp; the spectrophotometric measurements were made with a Beckman DK-1A unit.

Results and Discussion

The Donnan dialysis experiments were performed in the same general manner as in the previous chapter. The enrichments were for 30 min; the enrichment factor was calculated as the concentration in the receiver after the prescribed time divided by the

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Results and Discussion

The Donnan dialysis experiments were performed in the same general manner as in the previous chapter. The enrichments were for 30 min; the enrichment factor was calculated as the concentration in the receiver after the prescribed time divided by the

original concentration in the sample. When the receiver electrolyte was simple salt solution such as 0.1 M KNO_3, the sample pH had a marked influence on the enrichment factor. For example, at sample pH's of 2.5, 3, 3.5, and 4 the enrichment factors were 5, 6, 4.7, and 0.3, respectively, under the following conditions: receiver, 2 mL of 0.1 M KNO_3; sample, 100 mL of 2 x 10^{-4}M phosphate; enrichment time, 2 hr; membrane area, 1.9 cm^2. The same general results were obtained for arsenate. Obviously, such a system would have no analytical utility as the enrichment would vary from sample to sample.

When the sample solution is of a constant pH, the pH of the receiver also affects the enrichment factor. With a pH 3.6 sample and with receiver pH's of 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, and 6.0, the enrichment factors were 7, 7, 7, 7, 5, 5, 5.2, 5, and 5, respectively, under the same general conditions as above. Whereas the effect of sample pH was anticipated because of the relationship of pH to the charge of the phosphoric acid anions which would be present at equilibrium, the effect of receiver pH was surprising.

That the receiver pH influences the enrichment factor indicates that the process of Donnan dialysis is not purely diffusional. Thus, as was the case with

cationic systems, conditions apparently exist where the transfer rate is determined by kinetics.

The comparison to the cationic system further indicates that if the receiver solution were of low pH, the protonation of the anions attached to the fixed sites of the membrane would cause release and result in (A) more rapid enrichment and (B) an enrichment which is independent of sample pH. The data in Table 4 demonstrate that indeed this is the case.

Table 4

Influence of pH on the Donnan Dialysis Enrichment of Phosphate

Receiver pH	Sample pH	Enrichment factor*
1.5	2.0	2.8
1.5	3.0-10.0	7.0±0.03
3.5	4.0	6.3
5.2	4.0	4.9
5.2	6.9	3.9
5.2	9.2	3.3

*Ratio of receiver concentration after enrichment to the original sample concentration. Receiver: 2 mL of 0.1 M KNO_3 adjusted with HNO_3 or KOH. Membrane: 4.9 cm^2 P-1025. Enrichment time, 30 min.

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In fact, it was found that as long as the receiver pH was less than the pK of the weak acid (or lowest pK of a polybasic acid) the enrichment factor was constant.

When the optimum receiver is used with phosphate and arsenate samples, the resulting enrichment factor is independent of the test species concentration (i.e., in 30 min a 1.0 ppm phosphate sample can be enriched to 7.1 ppm and a 10 ppb phosphate sample, the lowest concentration studied, can be enriched to 71±2 ppb). Further, the results reported in Chapter 2 on the precision, effect of sample ionic strength, and effect of enrichment time were found to be applicable here. The enrichment was found to be independent of receiver ionic strength over a wide range, however. For example, the enrichment factor only varied from 6.9 to 7.1 with 0.2 M and 2.0 M KNO_3 receiver electrolytes, respectively.

Of the tested weak acids, only bisulfate did not obey the general rule. Sulfate also had a much lower enrichment factor than the other anions which were studied. Further, only sulfate interfered significantly with the enrichment of other conjugate bases of weak acids (see Table 6). Sulfate may interfere by reacting irreversibly with impurity sites on the membrane and thus lower the Donnan potential or by fixing very strongly to the exchange sites. At any rate in

concentrations expected in natural water samples and in typical wastewaters, the sulfate interference is not significant.

Table 6

Donnan Dialysis Enrichment of Mixtures of Weak Acids

Test anion	Added anion	EF*
Phosphate	10^{-5}M sulfate	7.1
	10^{-4}M sulfate	6.7
	10^{-3}M sulfate	4.8
Pyruvate	10^{-4}M sulfate	6.3
	10^{-3}M sulfate	4.7
Phosphate	10^{-3}M pyruvate	7.0
	10^{-3}M acetate	7.0

*Enrichment factor of the test anion. Sample pH, 5.2; other conditions the same as Table 4.

To establish which of the above observations are related to the weak acid nature of the investigated systems, selected experiments were repeated with chloride-containing samples. Using the conditions outlined in Table 4, 10^{-4}-10^{-5} M Cl^- samples were enriched by a factor of 7.0 in 30 min, and the results were independent of sample pH over the investigated range of 2-9. Unlike the weak acid cases, variation of the receiver pH over the range 2-6 did not change the enrichment factor (7.02 ± 0.03, 8 points). With mixed samples, the enrichments of phosphate and chloride were mutually independent. In addition, the presence of sulfate does not influence the enrichment of chloride.

These results are generally consistent with the previous observations. Chloride would be expected to weakly associate with the ion exchange sites, so pH effects should be negligible. Likewise, the presence of competing anions should not alter the enrichment. That the enrichment factor for chloride is the same as those for weak acids when the latter are transferred into a low pH solution supports a model for Donnan dialysis transfer in which the primary factor which determines the rate is the Donnan potential; with weak acids the primary rate can be decreased by the

exchange reaction at the membrane/receiver interface but not by diffusion of the test species.

Conclusion

Donnan dialysis enrichment of anions of weak acids can be accomplished if the receiver electrolyte has a pH less than the pK of the weak acid. Under these circumstances the enrichment factor is independent of sample pH over a wide range, independent of the sample concentration and directly proportional to time (up to about 4 hr). These results are important in that they make it feasible to apply Donnan dialysis to ion removal systems as well as to pretreatment of samples in chemical analysis. We have reported these conclusions elsewhere (12). A more detailed report of portions of this study is also available (13).

4. Applications of Donnan Dialysis to Trace Chemical Analysis in Water and Wastewater

In the previous chapters it was shown that Donnan dialysis can be used to perform ion enrichments in a manner which yields concentrations in receiver solutions which are directly proportional to the original concentrations in the samples. These results suggest that Donnan dialysis is a potential alternative to chemical methods of sample pretreatment and en-

richment. Summarized below is a study in which Donnan dialysis was applied to the determination of various metal ions, phosphate, and arsenate in selected surface water and sewage samples; included are comparisons to chemical pretreatments.

Experimental

The design of the experiments, treatment of the membranes, reagents, and instruments were as reported in previous chapters. The comparative techniques were taken from a compilation of standard methods (14).

In the dialysis experiments the grab samples were filtered through a coarse glass frit and used within 24 hr. In some cases, which are noted below, a filtration through a 0.45 micron millipore filter was also used. In most of the metal ion studies, spiked natural samples were used; in such cases the metal was added prior to the filtration step(s).

The phosphate and arsenate determinations by cathodic stripping analysis employed a procedure which we previously devised (15). The procedure is as follows:

The receiver solution was diluted to 4 ml by a pH 3 citrate buffer (1×10^{-4}M) which was 0.1 M in KNO_3. The solution was transferred to the electrochemical cell. After deaeration, 6 mg of $FeSO_4 \cdot 7H_2O$ were added. The glassy carbon electrode was introduced

and held at -0.2V during the final stage of deaeration.

The preconcentration step was initiated by applying 0.65V. Magnetic stirring was used to provide convection during both the preconcentration and stripping steps. After a prescribed electrolysis time, t_{el}, the accumulated Fe(III) phosphate film was stripped by application of a negative linear potential scan of 18 mV/sec. Between trials the electrode was held at -0.2V for 3 minutes to aid restoration of the original surface condition of the electrode. The peak at 0.05V was related to the phosphate concentration of the original solution with a working curve.

Results and Discussion

Figure 5 contains a working curve which was obtained from a combination of Donnan dialysis and cathodic stripping voltammetry. An arsenate working curve was prepared by the same procedure except that the peak current, i_p, was measured at 0.07V vs. SCE; again a linear plot was obtained, but the slope was 8.3 μA/ppm AsO_4^{3-}. The stripping peaks of phosphate and arsenate are too close together to permit direct simultaneous determinations. Mixtures can be studied (16), however, by first determining the total of the two, reducing the arsenate by a chemical method (17), and then determining the phosphate alone.

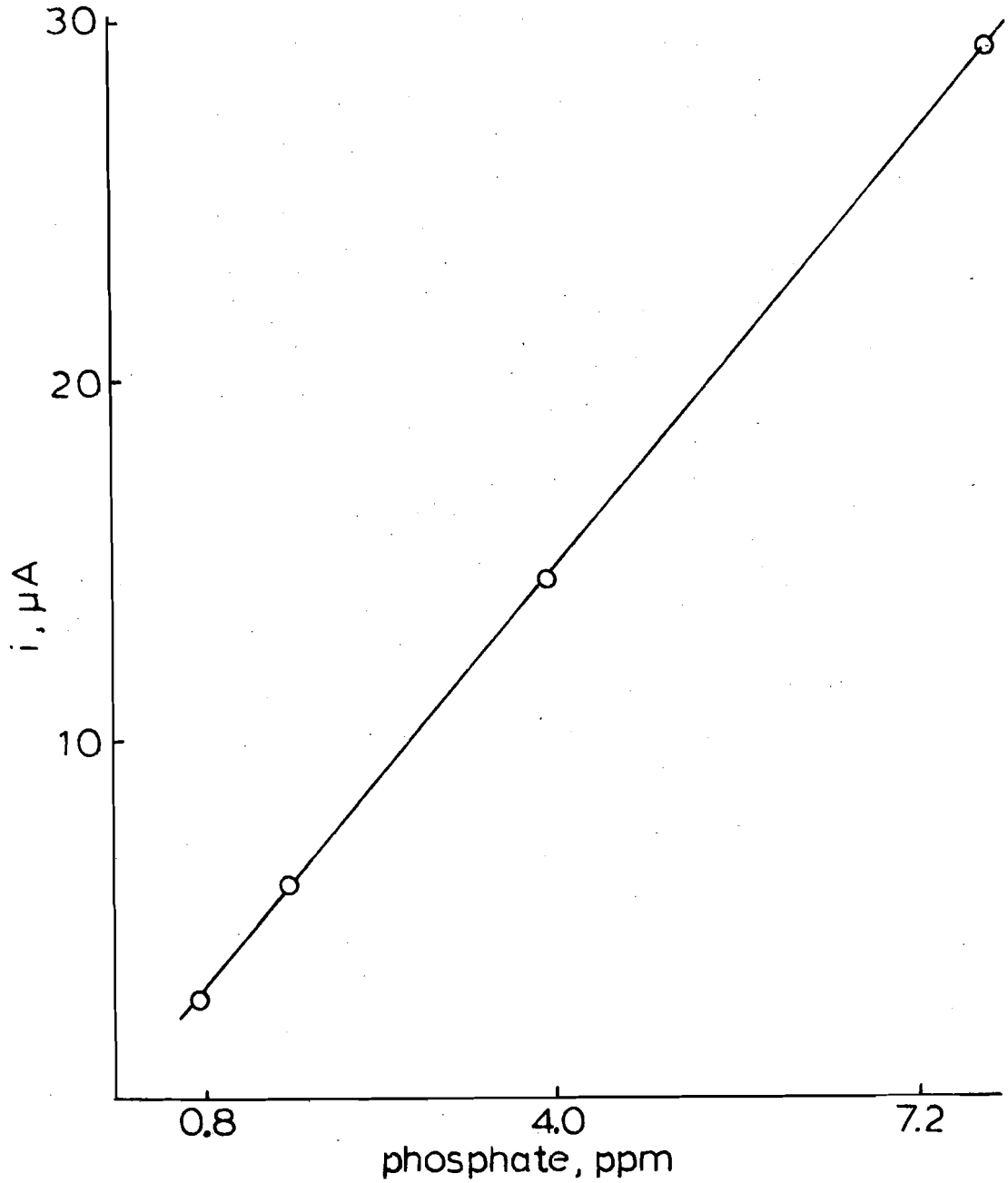


Figure 5. Cathodic Stripping Voltammetry Working Curve for Phosphate after Donnan Dialysis. Supporting Electrolyte: 0.1 M potassium nitrate, 8 mM chloroacetate, pH 3, 2.6 mM ferrous sulfate; electrolysis conditions: 10 min anodization at 0.5 volts followed by film stripping at 120 mV/sec scan.

The slopes of the working curves were unchanged when either 0.001% gelatin or 10 mg/L 1-octanol were included in the standard samples. This demonstrates that the membrane excludes these surfactants, which would otherwise lower the slope of a cathodic stripping working curve, and also shows that these species do not alter the Donnan dialysis rate.

The cathodic stripping procedure is very sensitive to pH and the Fe(II) concentration (15). Experiments were, therefore, performed to demonstrate that these parameters were not altered during Donnan dialysis of a variety of controlled samples. Using the receiver electrolyte which was described above, the pH was unchanged when samples containing 10^{-4}M phosphate in the pH range 3-9 were dialyzed for 1 hour. In fact, even with a receiver of 0.1M KNO_3 adjusted to pH 2.0, by H_2SO_4 the pH was constant during the dialysis experiments.

To test whether Fe(II) can transfer across the anion exchange membrane, 10^{-4}M Fe(II) samples were dialyzed for 4 hr. Subsequent spectrophotometric analysis of the receiver by the orthophenanthroline method (14) did not detect Fe(II).

Table 7 contains a summary of phosphate determinations in selected water samples by the molybdophosphoric (MP) and vanadomolybdophosphoric (VMP) acid

spectrophotometric methods and the Donnan dialysis/ cathodic stripping voltammetry (DD/DSV) technique.

Direct cathodic stripping analysis did not yield measurable peaks with any of the tested samples because of interferences. This demonstrates a major utility of Donnan dialysis.

The tabulated results show good agreement among the methods; they yielded statistically identical results at the 0.05 probability level by applying the F-test to a multiple group experiment. Using the cesspool sample and performing 5 trials by each method, the calculated F, 2.60, was smaller than the tabular value, 3.74, at that probability level.

Table 7

A Comparison of Donnan Dialysis/Cathodic Stripping to Spectrophotometry for Phosphate Determinations

	mg PO_4^{3-}/L		
Sample	VMP	MP	DD/CSV
1	0.069	0.067	0.065
2	0.138	0.111	0.125
3	0.072		0.065
4	12.4	12.2	12.3
5	11.1	11.0	10.5
6	3.13		3.08

Samples: 1, Big Muddy River; 2, Murphysboro Lake; 3, Campus Lake, SIU; 4, septic tank run-off; 5, cesspool water; 6, Chemistry Department, laboratory effluent.

In order to evaluate the applicability of the DD/CSV method to the determination of arsenate in mixtures with phosphate, 0.100 mg AsO_4^{3-}/L was added to sample 1. After dialysis, determination of the total phosphate and arsenate, chemical reduction, and determination of phosphate alone, a recovery of arsenate of 90% was calculated.

It should be noted that the DD/CSV approach only responds to anionic phosphate (and arsenate) or species in equilibrium with an anionic form since phosphate in other chemical states will not pass through the membrane. Thus, in addition to making a matrix-sensitive technique such as cathodic stripping voltammetry applicable to real samples without chemical pretreatment, Donnan dialysis is capable of performing certain speciation studies.

Metal ions at the trace level are commonly determined by pulse polarography and anodic stripping voltammetry. As these methods are highly susceptible to interference by surfactants, electrochemically active organic compounds, and complexing agents a digestion procedure is generally used prior to performing the electrochemical experiment. Unfortunately digestions may invalidate the results by introduction of metal impurities or by volatization of metals

present in the sample. In addition, a prior digestion will finally result in the determination of the total metal in a sample rather than the free metal ion concentration. In many cases the latter value is preferable.

An alternative to a digestion is a separation. In Chapter 2 we have demonstrated that Donnan dialysis is in some ways a superior separation method to the commonly employed columnar ion exchange and solvent extraction methods. A comparison of Donnan dialysis to digestion methods was, therefore, made.

Figure 6 contains a pulse polarogram of a typical sample of sewage taken from the outfall of the chemistry building at Southern Illinois University-Carbondale. When the filtered sample was directly determined (after addition of the supporting electrolyte and removal of dissolved oxygen), several peaks were present; however, a 15 min dialysis eliminated all peaks except the one at -0.98V vs SCE which was identified by standard addition as being due to 1.2×10^{-7}M Zn^{2+}.

In retrospect the Zn^{2+} could have been determined in the original, untreated sample in that the peak potential was unchanged by the Donnan dialysis step; but generally this would not be reliable as the potential of Zn^{2+} reduction was found to be highly

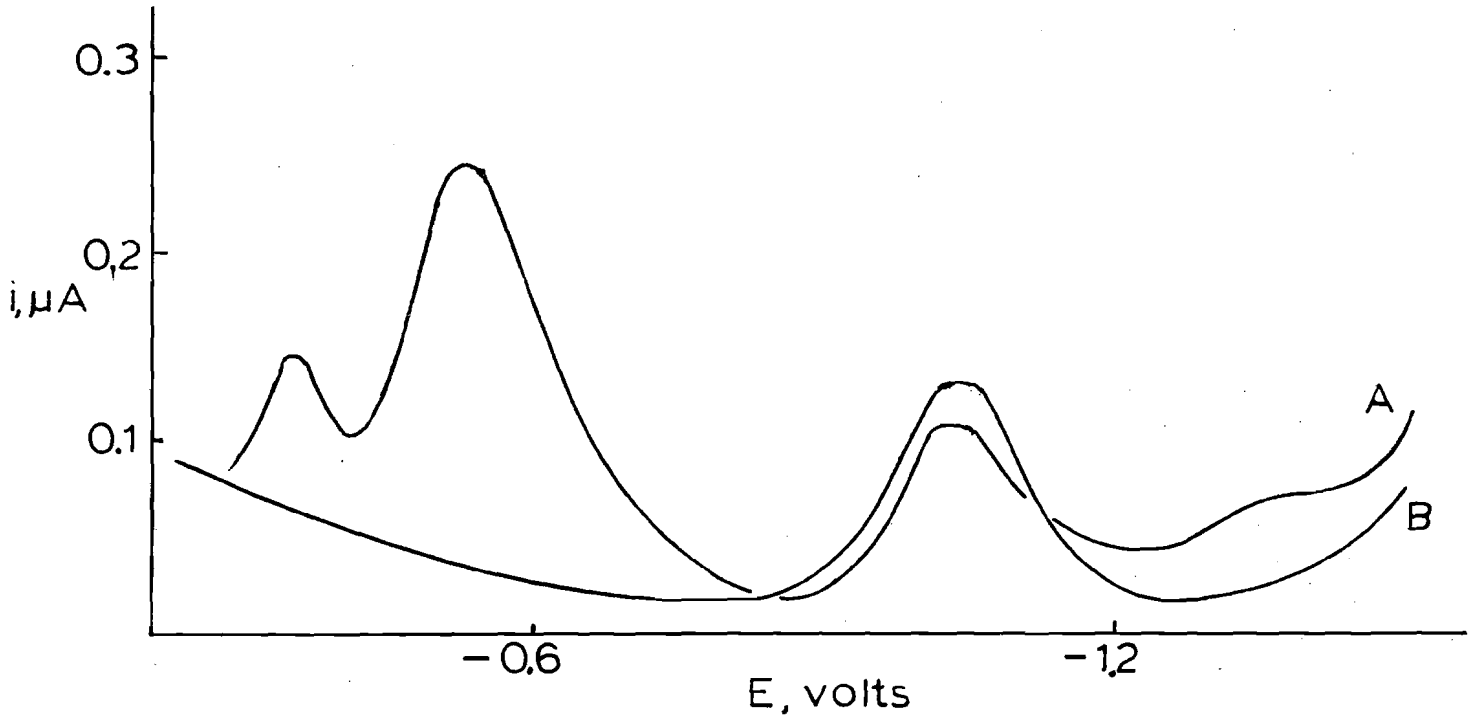


Figure 6. Effect of Donnan Dialysis on the Differential Pulse Polarogram of a Sewage Sample. A, filtered sample plus 0.2 M $MgSO_4$, 0.1 mM $Al_2(SO_4)_3$; B, dialysate after 15 min into the above electrolyte.

dependent on the nature of the sample matrix. For example, in another sewage sample the Zn(II) reduction potential was at -0.830 V vs SCE prior to Donnan dialysis; upon transferring it into the 0.2 M $MgSO_4$, 5 x 10^{-4}M $Al_2(SO_4)_3$ receiver, the peak of the subsequent pulse polarogram was at -0.980V, which is the normal potential for the Zn(II) reduction in this electrolyte.

An acid digestion procedure was also used to attempt to clarify the polarogram shown in Figure 6. The sample was made 20% by volume in HNO_3, steamed to near dryness, and diluted to the original volume with the Mg, Al electrolyte. The polarogram of the digested sample showed a 55% loss of Zn and a somewhat higher background current, but the peaks other than Zn in Figure 6 were absent. Ammonium persulfate and hydrogen peroxide digestions were unsuccessful in terms of clarifying the polarograms.

In addition to yielding a cleaner sample and exhibiting much less sample loss, the Donnan dialysis sample treatment was significantly more rapid than the chemical treatment. The total treatment and analysis time was about 1-2 hr per sample for the former, compared to 4 hr per sample for the latter method. The time range for Donnan dialysis occurs

as a result of the varying degree of enrichment which may be desired. A 15 min dialysis results in an enrichment factor of about unity, i.e., the concentration of the metal in the receiver after that time is the same as the original concentration in the sample; in this case Donnan dialysis is only used to separate the metal from the sample matrix.

In Figure 7 is shown the effect of a Donnan dialysis treatment of a lake water sample which was analyzed by pulse polarography. In this case the sample was filtered with 0.45 micron millipore as well as a glass frit, and the sample was spiked with Pb, Cd, and Zn. Apparent enrichment factors were calculated by dividing the peak currents in the final solution by the peak currents in the original sample. The latter were the best estimates above the background. With a 1 hr dialysis, the apparent enrichment factors were: Pb (7.4), Cd (9.3), and Zn (11.3). The true enrichment factors were determined by dialyzing standard solutions under the same conditions. The resulting values were: Pb (8), Cd (10), and Zn (10).

The differences between the true and apparent enrichment factors can be due to a matrix effect affecting either the peak current in the undialyzed sample or the rate of Donnan dialysis. If the latter

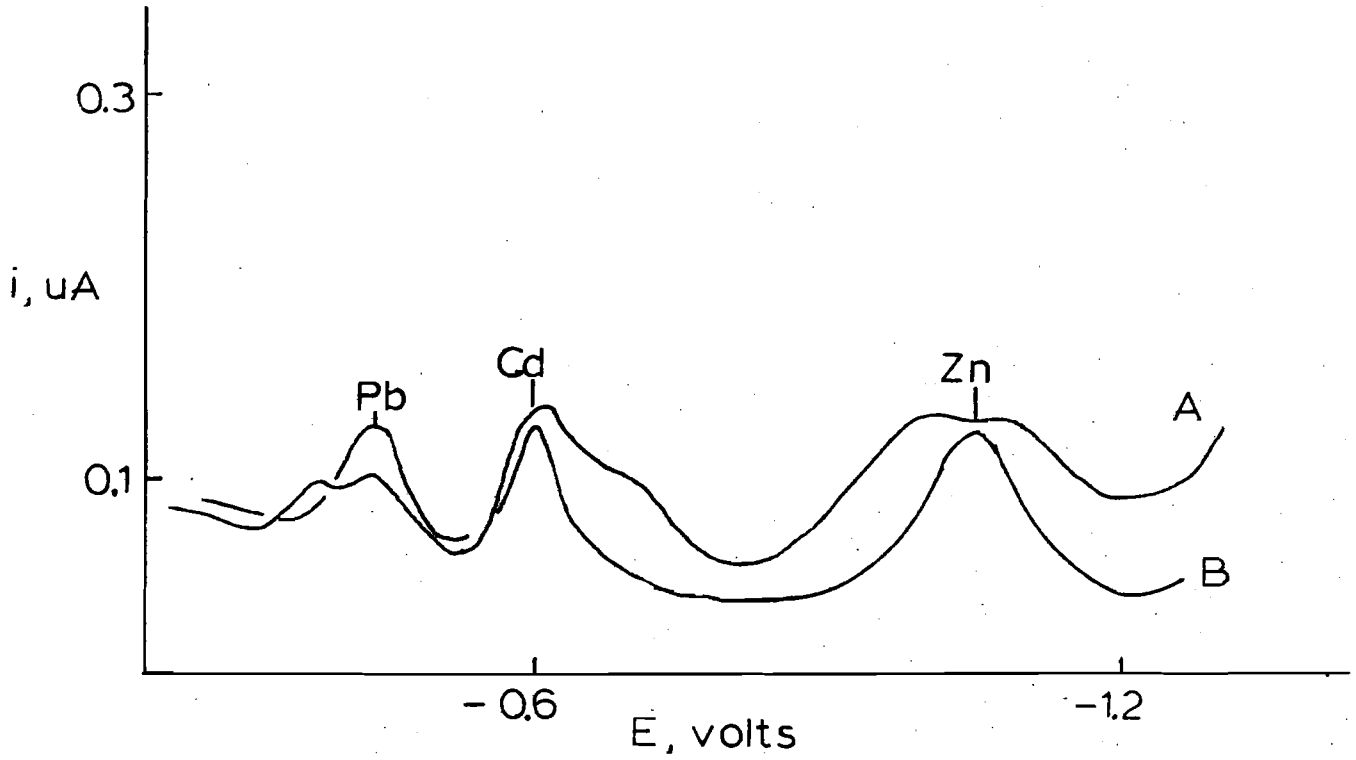


Figure 7. Effect of Donnan Dialysis on the Differential Pulse Polarogram of a Lake Water Sample. Sample was spiked with Pb, Cd, and Zn. Conditions same as in Figure 6.

were true, Donnan dialysis would not be a useful technique. Fortunately, it was demonstrated that surfactants in the sample were affecting the peaks in the untreated samples; typical data are shown in Table 8. The tabulated effects by gelatin are in the correct order and magnitude to account for the enrichment factor differences.

Table 8

Effect of a Surfactant on the Pulse Polarography Peak Current

% gelatin added	Pb current,μA	Cd current,μA	Zn current,μA
0	0.043	0.049	0.051
0.002	0.046	0.046	0.042
	0.051	0.044	*
	0.053	0.042	*
	0.060	0.035	*

6.0×10^{-7}M Zn(II), 6.8×10^{-7}M Cd(II), 6.3×10^{-7}M Pb(II)

*Peak could not be reliably measured.

Another possible approach to the electrochemical determination of trace metals in water is to use anodic stripping voltammetry. In this case the metals are enriched into Hg; subsequently the deposited metals are reoxidized by applying a positive-going potential scan. Since the organic compounds would not be enriched, this approach can theoretically yield an improved signal-to-background recording on samples like those shown in Figures 6 and 7. However, with such samples stripping peaks were not successfully developed. Apparently during the 30 min exposure of the Hg electrode so much adsorption of surfactants occurred that the surface became passivated. When Donnan dialysis was used prior to the anodic stripping voltammetry experiment, the Pb, Cd, and Zn peaks were developed at the expected heights (±8%).

Conclusion

Donnan dialysis can be used for treatment of water samples prior to employing trace chemical analysis procedures. The method is seemingly superior to chemical digestions for many cases although it should be noted that the subsequent analyses will only be for the concentrations of the free metal ions in the original samples. The dialysis approach also has some advantages over separation methods such as

solvent extraction, especially for electroanalytical applications which are preferably performed in aqueous solution.

5. Design of Voltammetric Ion Selective Electrodes

Membrane-clad voltammetric sensors for low molecular weight neutral species, such as gases dissolved in water have found wide application in water resources research. The most common of these is the oxygen sensor. Comparable designs for the determination of ionic species have not been previously reported, but the concept has been recognized as worthy (18,19).

As an extension of our use of ion exchange membranes to perform Donnan dialysis enrichments, we have designed and tested a voltammetric ion selective electrode for nitrate.

Experimental

The instrumentation consisted of a three electrode polarograph which was constructed with Teledyne Philbrick Model 1027 operational amplifiers (although any commercial polarograph, even the most inexpensive,could be used) and a Hewlett Packard Model 15101B strip chart recorder. The chemicals were ACS Reagent Grade and were used without further purification. Because of the known

effect of aging, the electrolytes were prepared from a 0.1M $ZrOCl_2$ stock solution which had been stored for at least 3 weeks.

The ion exchange membranes and the polyvinyl acetate and polyvinyl alcohol neutral membranes were obtained from RAI Research Corporation, Hauppauge, Long Island, New York. The ion exchange membranes were pretreated by the general procedure of Blaedel and Kissel (5) except that they were stored in 0.1M KCl, 0.01M $ZrOCl_2$ prior to use.

The membrane-clad voltammetric sensors utilized Ag/AgCl reference, platinum counter, and constrained mercury column indicator electrodes. The system was constructed by cementing a 5 mm outer (2 mm inner) diameter glass tube into one with a 12 mm outer diameter with Torr Seal low vapor pressure resin, Varian Association, Vacuum Division, Palo Alto, California; the tubes were concentrically placed. The reference and counter electrode wires were also cemented into the assembly. The resin face and outer tube of the sensor were machined at a 45° angle; the mercury tube was left planar. A diagram is shown in Figure 8.

A pair of 5 mm diameter disks of Whatman no. 40 (medium) filter paper were placed over the end of the mercury tube and overlapped the machined resin face;

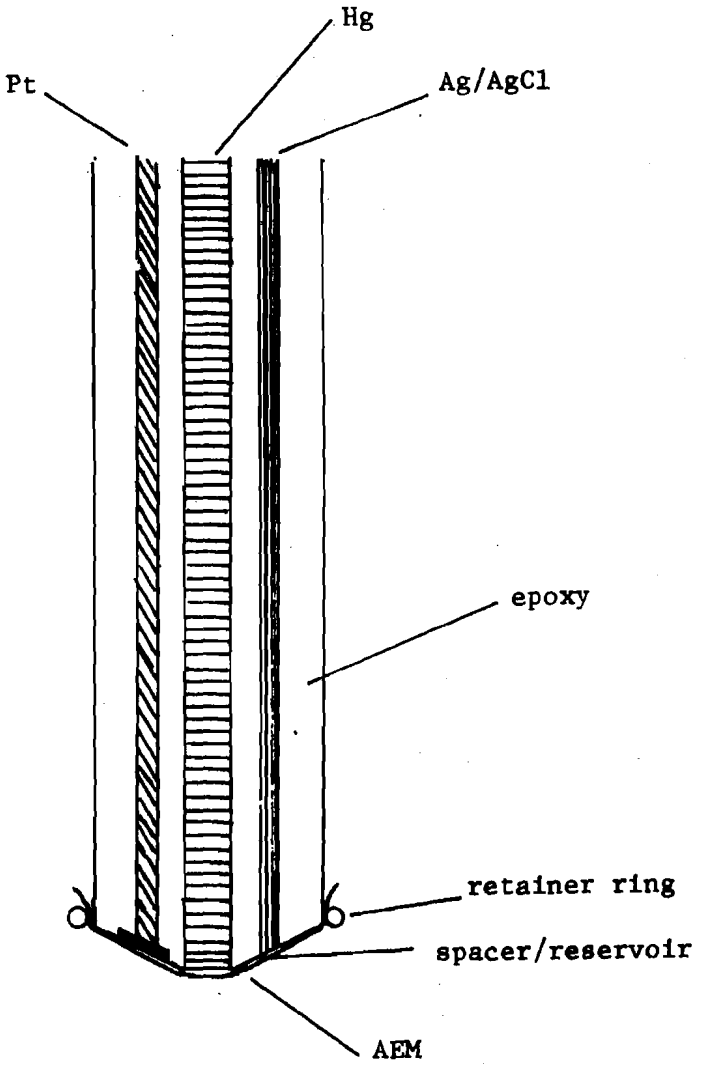


Figure 8. Design of the Voltammetric Ion Selective Electrode.

prior to assembly they were impregnated with the KCl, $ZrOCl_2$ electrolyte. The paper served as the constraint for the mercury and as a spacer. A few excess drops of electrolyte were placed on the paper and an ion exchange membrane was firmly drawn over the entire end of the assembly. The membrane was fixed in place by Teflon tape and a small plastic hose clamp. Mercury was poured into the inner tube and electrical contact was made by inserting a platinum wire. It should be noted that the electrolysis cell thickness in this design is determined by the thickness of the compressed paper spacers. The length of the complete assembly is about 12 cm.

The assembly was stored in supporting electrolyte between experiments. As co-ion penetration occurs extensively with a high ionic strength solution on each side of the membrane, this step regenerates the inner solution and removes the electrolysis products.

Results and Discussion

Previously we reported an electrochemical method for the determination of nitrate which used an anion exchange membrane to isolate the sample from the electrochemical cell (1). In this case a timed enrichment by Donnan dialysis was used prior to the electrochemical analysis. The analytical procedure used the reduction of nitrate at a mercury electrode

in the presence of La(III) for the sensing reaction.

The above method had certain limitations for applications which would require the experiment to be performed by technicians. The La(III) catalyst passivated the Hg electrode after each trial, and the electrochemical method, linear scan voltammetry, is not well known in applied laboratories and utilizes relatively sophisticated instrumentation. The design presented herein can be adapted for use with instruments used in conjunction with the oxygen sensor.

To eliminate the problems of the La(III) catalyst, several alternative systems were explored. The well known U(VI) catalyst (20) gave a limited linear working range. The Cu, Cd catalyst for electrochemical reduction of nitrate (21) was not found to be suitable for inclusion in the sensor as the analytical current is measured above that of another reduction process. Zr(IV) has frequently been used as the catalyst for nitrate reduction (22) and was found to be suitable for the present system.

Figure 9 shows the linear scan voltammogram for the reduction of nitrate at Hg in the presence of the Zr(IV) catalyst. The process was found to be an 8 electron reduction to NH_4^+. The presence of dissolved oxygen in the sample did not affect the

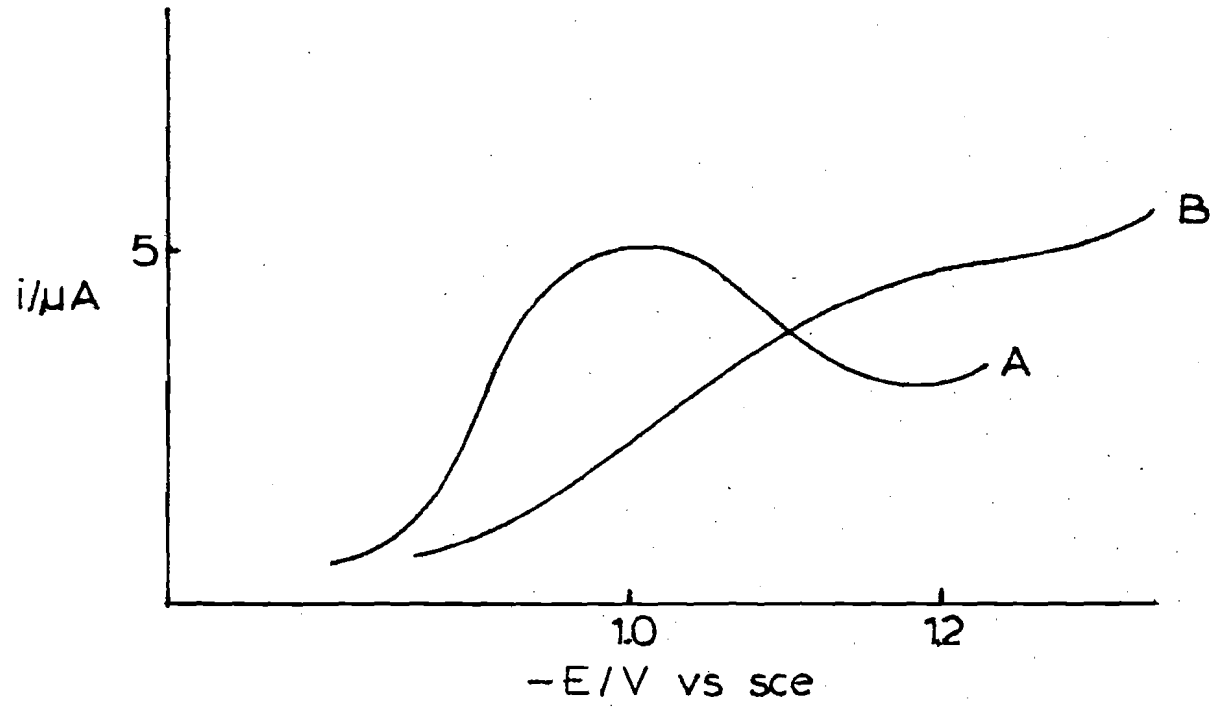


Figure 9. Linear Scan Voltammograms of Nitrate at Mercury Electrodes in the Presence of Zr(IV). A, hanging drop; B, paper constrained mercury column.

nitrate current but does increase the background.

In the sealed system, a typical Hg electrode (such as a dropping electrode, stationary drop or Hg pool) cannot be used, so several alternative indicators were tested. These were: graphite; wax-impregnated graphite; mercury-coated graphite, platinum,and silver; and silver. They were tested with all of the above-mentioned catalysts. In every case a reduction current for nitrate failed to be clearly developed prior to the reduction of the supporting electrolyte; thus, efforts were made to find a physically useful configuration of a pure Hg surface.

Figure 9 includes a voltammogram for the nitrate reduction at a constrained Hg column. Of the constraining materials tested (neutral membranes, glass frit, and filter paper),only the latter produced a useful response. Therefore, the electrode design shown in Figure 8 was employed. It should be noted that the drawn out voltammogram (Figure 9) with the constrained Hg electrode is a result of a high ohmic resistance. Nevertheless at a potential of -1.25 V a good ratio of the nitrate reduction current to the background current is obtained.

In Figure 10 are shown current-time curves which are obtained when the membrane-clad sensor is dipped into blank and nitrate-containing samples and the above electrolysis potential is applied. Unlike the response characteristics of the commercial oxygen electrodes, a steady state current is not obtained. Working curves must, therefore, be obtained by measuring the net current at a prescribed time after introduction of the sensor into the standard solutions.

Working curves which were obtained at two prescribed times are shown in Figures 11 and 12. The use of the 8 min current value is only necessary at concentrations below about 10 ppm NO_3^-, but if it is selected, the linear range of the sensor extends from 10^{-2}-10^{-5}M NO_3^-. The 2 min measurement is likewise useful from 10^{-2}-10^{-4}M NO_3^-.

With the 8 min measurement, the standard deviation of 5 replicate blank samples is 10 nanoamperes. The detection limit, using the criterion of that concentration which yields a signal of twice that of the blank uncertainty, is 6.7×10^{-6}M NO_3^-.

The major limitation of the electrode design in Figure 8 is the lack of a steady state current, which is a result of consumption of H^+ during the measurement. The solution to this problem is to develop an

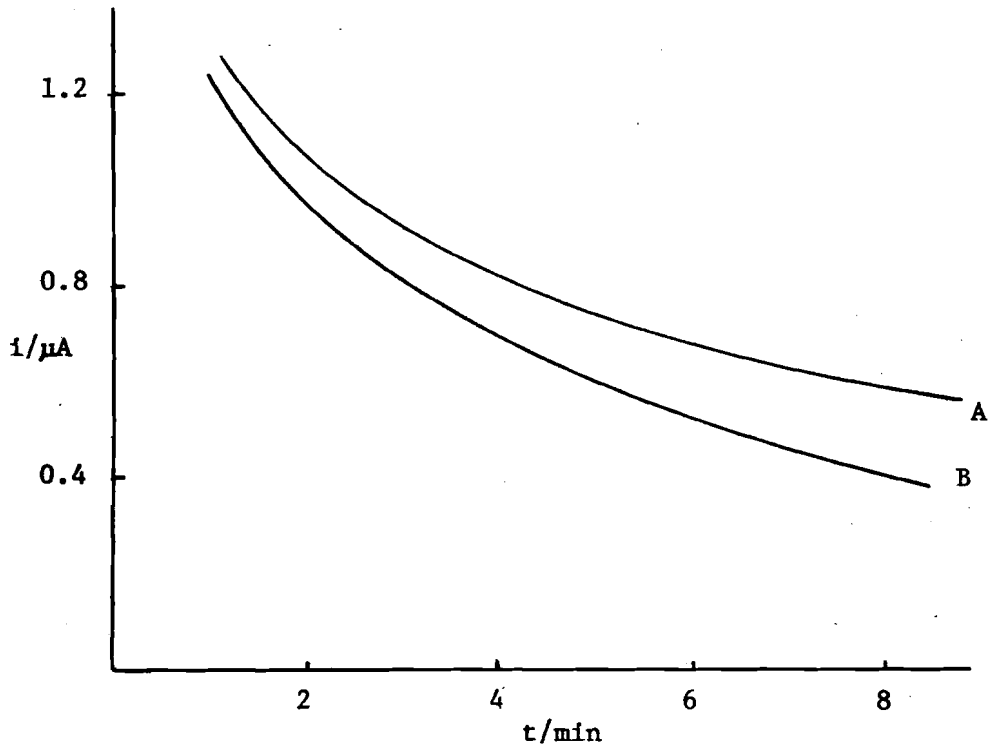


Figure 10. Current-Time Behavior of the Voltammetric Ion Selective Electrode for Nitrate. A, 0.01 mM nitrate sample; B, distilled water blank.

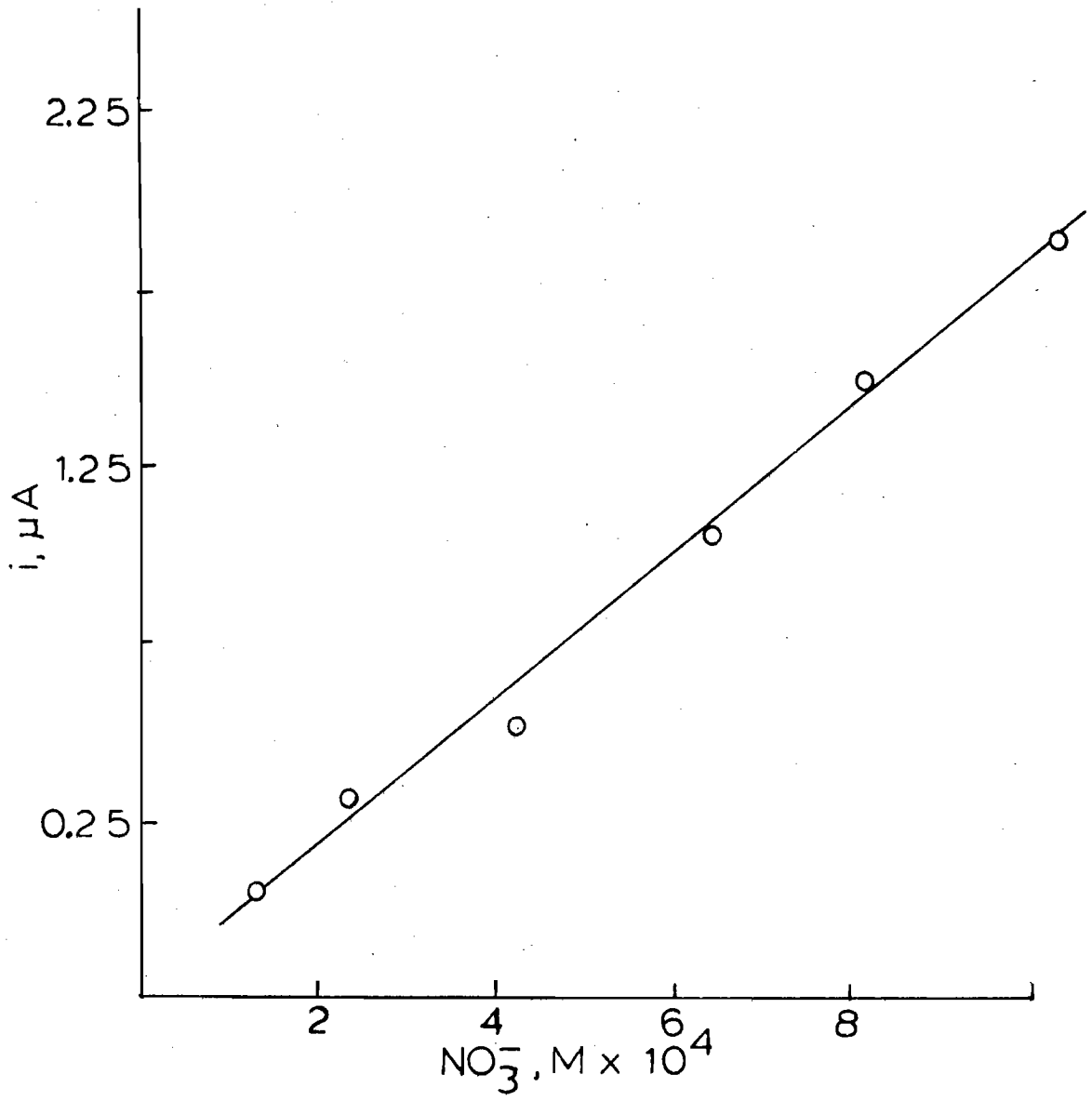


Figure 11. Voltammetric Nitrate Electrode Working Curve with a 1 Minute Current Sampling Time.

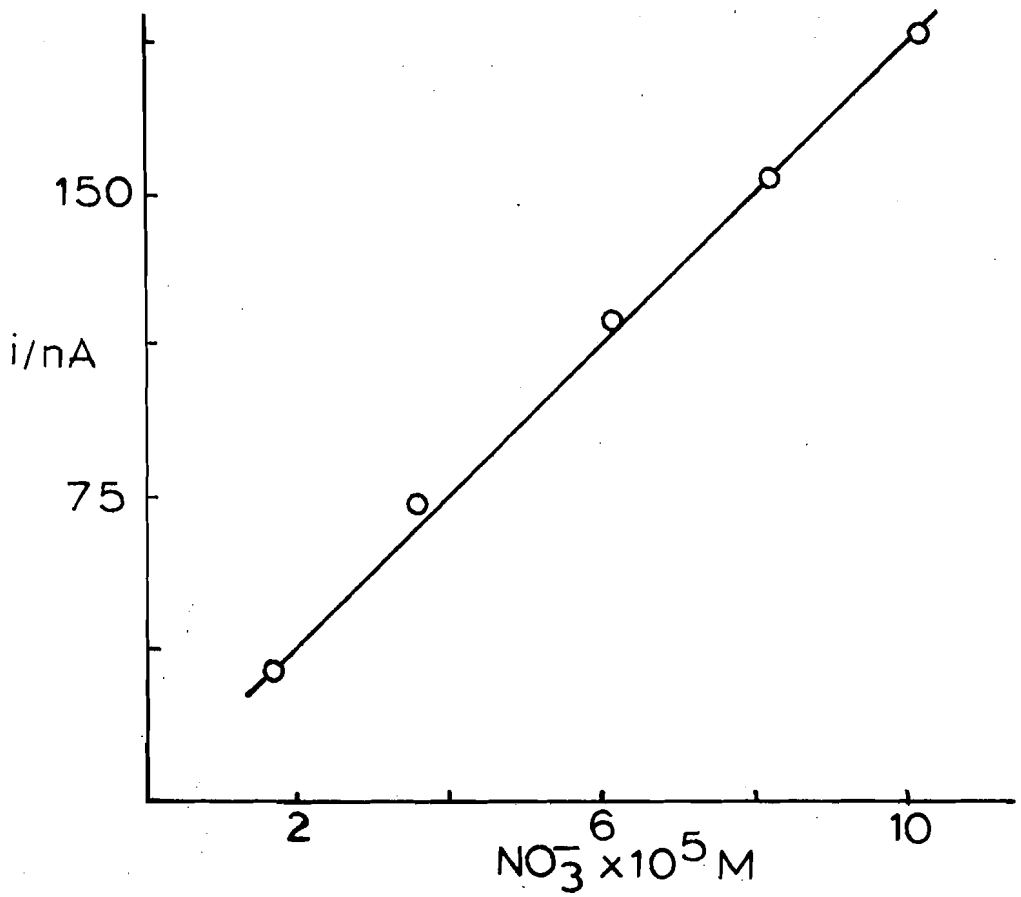


Figure 12. Voltammetric Nitrate Electrode Working Curve with an Eight Minute Current Sampling Time.

improved catalyst.

Molybdenum cysteine complexes are known to be reasonable analogs of the enzyme nitrate reductase and were, on this basis, selected for investigation as electroreduction catalysts. Complexes of Mo(VI), Mo(V) and their reduction products--either Mo(III) or Mo(IV)--were prepared by known procedures (23,24). Linear scan voltammograms at Hg electrodes were not affected by the presence of nitrate. When the solutions were allowed to stand for 24 hr prior to the electrochemical experiment, nitrate effects were observed. The reaction is too slow for application to a membrane-clad system.

The investigation of possible molybdenum catalysis did result in a significant analytical finding. Figure 13 shows linear scan voltammograms of Na_2MoO_4 in a 0.1M KCl, 0.01M HCl electrolyte in the presence and absence of nitrite. The peak at -0.9 V, which appears only in the presence of nitrite, is directly proportional to concentration of that ion in the range 10^{-2}-10^{-5}M NO_2^-. Even in the presence of 1000-fold excesses of NO_3^-, the analytical current is unaffected. As the response is immediate, the system should be useful for the construction of a voltammetric ion selective electrode for nitrite.

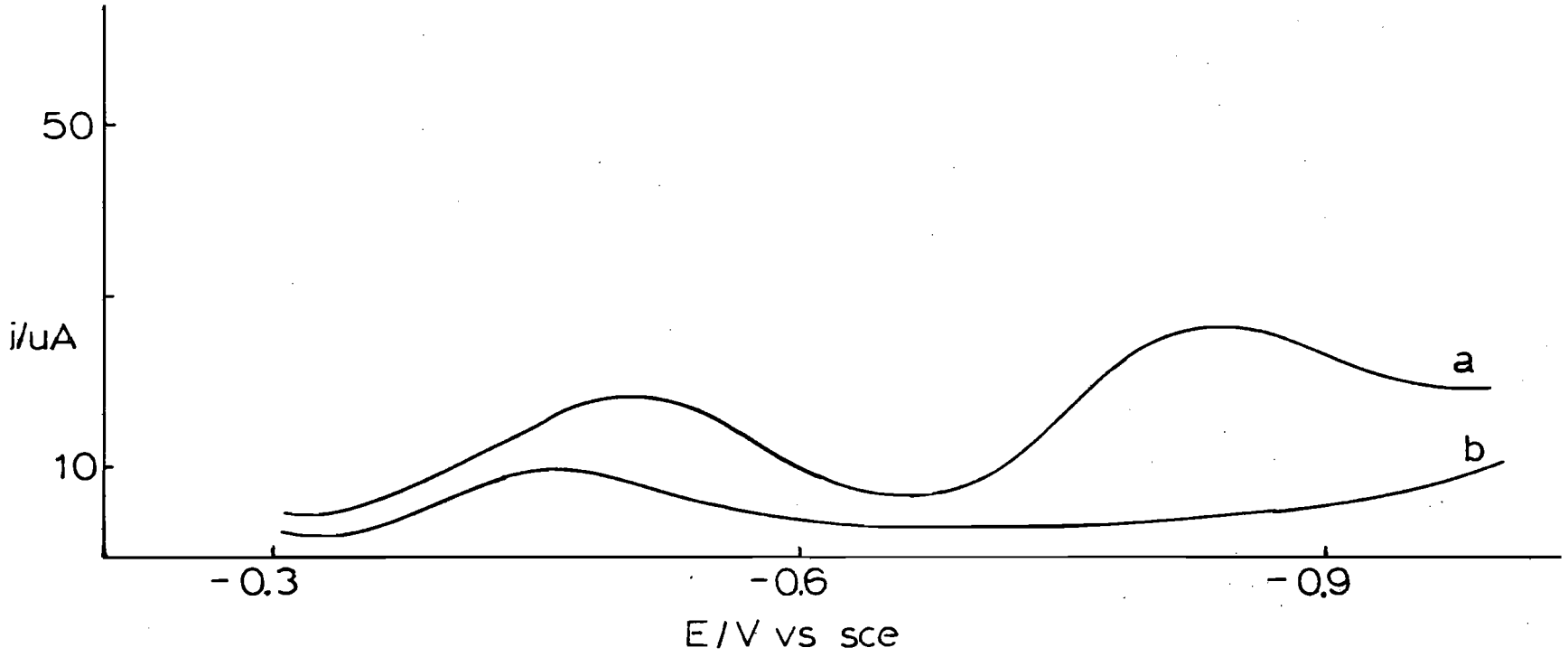


Figure 13. Molybdenum-Catalyzed Electrochemical Reduction of Nitrite. a, linear scan voltammogram of 6 mM nitrite in 1 mM sodium molybdate, 0.1 M KCl at pH 2; b, same as above except no nitrite.

6. Comparison of Electrodialysis to Donnan Dialysis

Electrodialysis is a common method for removing salts from samples. Because the method is somewhat similar to the Donnan dialysis procedures reported herein, a comparison was performed in order to help in the evaluation of the long term potential of Donnan dialysis.

The major concern was to determine whether the rate of Donnan dialysis is comparable to that of electrodialysis. Since the latter method is already in use for water treatment, data on the relative rates would indicate whether Donnan dialysis may be economically practical in water treatment.

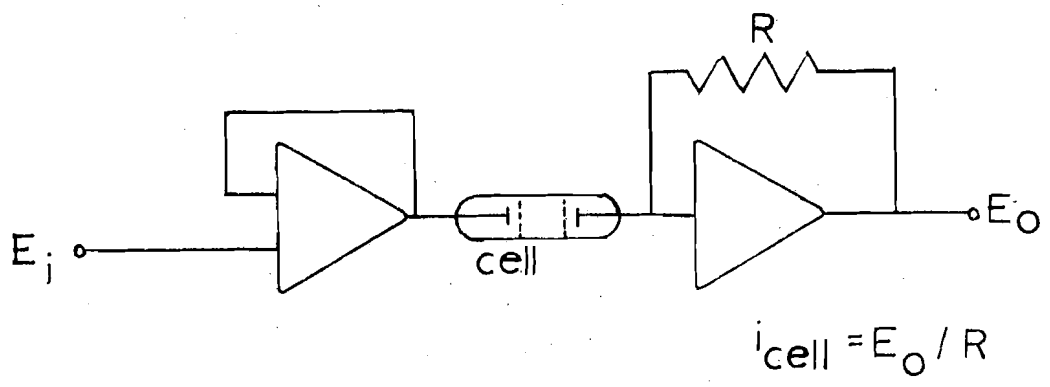
Experimental

Electrodialysis experiments were performed with both potentiostatic and galvanostatic operation. In each case the instrument was constructed with vacuum tube operational amplifiers which are capable of 100 V outputs. The potentiostatic operation was performed by placing the 3-chamber dialysis cell between the output of a voltage follower and the input of a current follower. The galvanostatic experiments were accomplished by inserting the cell in the negative feedback loop of an operational amplifier; this approach results in a dialysis current which is

equal to a preset input current to the amplifier and is unaffected by the resistance of the cell (see Figure 14). The 3-chamber dialysis cell consisted of receiver compartments, which contained Pt electrodes and various salt solutions, and a sample compartment; ion exchange membranes separated them. The ion exchange membranes were P-1010 and P-1025, as described earlier. The cell and sample volumes, the membrane areas, and the overall geometry were kept as similar as possible to the Donnan dialysis setup of Chapter 2 so that the resulting enrichments could be compared.

Results and Discussion

Preliminary experiments were performed in the galvanostatic mode as it should be more like Donnan dialysis than the potentiostatic mode. Using a 1 mA current, 10^{-3}M KCl receivers, and Na^+-containing samples, the following observations were made: the concentration of Na^+ in the receiver was directly proportional to dialysis time and to the original Na^+ in the sample; repeated trials on the same sample yielded direct proportionality between the current and the enrichment factor; and the results were independent of the concentration of the KCl receiver solutions. These results simply demonstrate the veracity of the galvanostatic mode



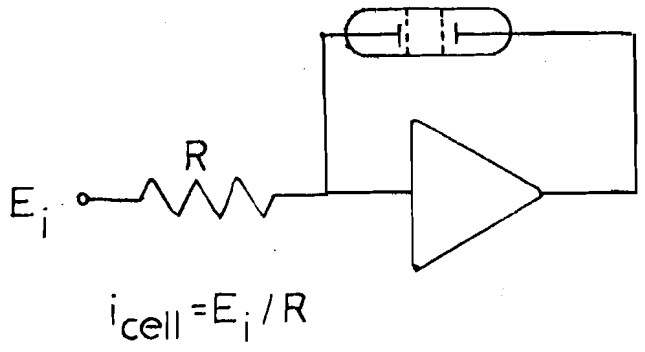


Figure 14. Operational Amplifier Electrodialysis Instrumentation for Galvanostatic and Potentiostatic Modes.

and the simple instrument design which was employed. Compared to another recently reported electrodialysis galvanostat (25), the design in Figure 14 is advantageous in terms of simplicity.

The above results also indicated that galvanostatic electrodialysis may be a useful analytical enrichment and separation technique; however, as shown in Table 9, the method is subject to interference by all ions of the same charge sign as the test species.

Table 9

Galvanostatic Electrodialysis Enrichment of Mixed Samples

Sample	Na enrichment factor*
1.0×10^{-4}M NaCl	6.2
1.0×10^{-9}M NaCl, 1.0×10^{-4}M KCl	5.0
1.0×10^{-4}M NaCl, 1.0×10^{-3}M KCl	1.7

*200 mL samples 10 mL receiver; 30 min dialysis at 1mA

Comparable Donnan dialysis experiments (8,9) showed an independence of enrichment factor on sample ionic content (other than the test ion) up to the 0.01M - level. Hence, galvanostatic electrodialysis

is relatively disadvantageous. By using an internal standard, a standard addition approach, or exhaustive dialysis, electrodialysis can be applied since the effect of sample ionic content would be corrected; the extra effort would only be worthwhile when the sample ionic strength is too high for Donnan dialysis applications.

An attempt to overcome the effect of mixtures on electrodialysis enrichments by using potentiostatic operation was made. The transfer rate, exhibited by the dialysis rate, was still a function of the ionic content and was in addition dependent upon the receiver electrolyte concentrations. This approach was useful in that exhaustive dialyses could be easily made because the drop in current when the sample becomes depleted of ions acts as an indicator.

The enrichment factor for Cu(II) was determined by galvanostatic electrodialysis. Eleven 200 mL samples of 10^{-4}M $CuCl_2$ were dialyzed for 30 min each at 1.0 mA across 6 cm^2 membranes. The final concentrations in 5 mL receivers (10^{-4}M KCl) were determined by atomic absorption spectrometry. The average result was 1.03×10^{-3}M Cu (enrichment factor, 10.3) with a relative standard deviation of 6%. Under these conditions (except a Mg, Al receiver as noted

in Chapter 2), the Donnan dialysis enrichment factor is 7.0 with a relative standard deviation of 8%.

It can therefore be concluded that electrodialysis is a faster process. Certainly the use of larger membranes would increase the enrichment rate of Donnan dialysis, but larger currents which would enhance electrodialysis in the same manner (direct proportionality to current for the latter; direct proportionality to membrane area for the former) are just as feasible. As the enrichment factor and the rate of ion removal from a sample are directly related, it is apparent that Donnan dialysis is not advantageous, in general, relative to electrodialysis; and, in fact, for most water treatment problems it would seemingly be a poor choice.

Conclusions

Donnan dialysis was shown to be superior to electrodialysis as a means of accomplishing analytical enrichments of ions but was found to be less suitable for applications in which the objective is to remove (or replace) certain ions from water samples. A simple instrument for galvanostatic electrodialysis was developed and tested.

7. An Evaluation of Electrochemical Methods for Continuous Removal of Anions from an Electrolyte

The proposed method for continuous separation of ions from a water system was to first use dialysis to transfer the ions into an electrolyte and then to deactivate them either by electrochemical reduction or by plating them as an insoluble salt on an electrode; subsequently the salt could be mechanically removed. The present study indicates that reduction of nitrate to ammonia may be practical but that plating of phosphate onto a lead electrode is not feasible for the quantities anticipated.

Experimental

The nitrate study used the same equipment, reagents, and general procedures as described previously. The mechanistic study of the behavior of lead in phosphate medium was performed with a PAR 170 Electrochemistry System (Princeton Applied Research).

The Pb electrodes were either 99.999% pure wires (Ventron Alfa Products, Beverly, Mass.) or ca. 1% Pb amalgams. The latter were prepared by dissolving Pb in Hg under a controlled N_2 atmosphere in a Vacuum Atmospheres Company unit.

Results and Discussion

The reduction of nitrate was studied at a mercury electrode in the presence of a $ZrOCl_2$ catalyst. Controlled potential electrolysis at -1.1 V was performed to determine the n-value. Solutions were electrolyzed until the current dropped to that of the Zr(IV), KCl electrolyte (about 40 min), and the data were evaluated by integration of the i-t curve and comparison to the cell constant. The n-values which were found were 7.8, 7.6, and 7.6 electrons, respectively, for the following three solutions: 10^{-2}M Zr(IV), 10^{-4}M NO_3^-; 10^{-2}M Zr(IV), 10^{-3}M NO_3^-; and 10^{-3}M Zr(IV), 10^{-4}M NO_3^-. Head-space gas chromatography showed NH_3 as the major product (an 85% yield). The data demonstrate that the primary pathway is an 8 electron reduction to NH_3. The experimental deviation is probably due to incomplete electrolysis and some loss of NH_3 from the cell.

The above process was unaffected by the presence of dissolved oxygen; the same mercury surface could be continuously used with no loss of efficiency; and the build-up of NH_4^+ did not affect the electrolysis. Thus, the method of Donnan dialysis coupled to electroreduction appears to be applicable to the continuous removal of nitrate. The only necessary

chemical step would be to occasionally add HCl in order to replace the H^+ consumed in the electrochemical reaction and the Cl^- which is lost in the Donnan dialysis exchange. Eventually (when NH_4^+ approached 0.1M) the electrolyte would have to be regenerated by adding sufficient base to evolve NH_3 and then re-acidifying to dissolve the catalyst and restore the solution to the pH 2 level at which the electrolysis is efficient. Unfortunately, as discussed in Chapter 6, the Donnan dialysis procedure limits the overall utility of this ion removal system.

The proposed method for deactivation of phosphate was to oxidize a lead electrode to form a sparingly soluble phosphate salt film in the presence of that anion; this step would be subsequent to Donnan dialysis.

Preliminary linear scan voltammograms which were obtained at both pure lead and dilute lead amalgams indicated that the electrode surface was passivated by the salt film. The mechanism of the film formation was studied by a well known potentiostatic technique (26) in the hope that by understanding the mechanism the electrolysis could be modified in order to avoid the passivation.

By fitting experimental current-time curves to theoretical predictions for various film formation mechanisms, it was established that the process was a 2-dimensional progressive nucleation and growth of

$PbHPO_4$; the passivation was shown to be caused by a single monolayer on the amalgam electrode. At pure Pb surfaces, about 10 monolayers could be deposited. Neither case permitted deposition of films of a useful thickness for the present study. Variation of the pH and electrolysis potential did not alter the results.

Conclusion

The reduction of NO_3^- to NH_4^+ at Hg in the presence of a Zr(IV) catalyst is a useful means of deactivating that anion. Deposition of phosphate as a film on a lead electrode does not give sufficiently thick films to serve as the deactivation step in a continuous removal scheme.

8. Summary and Applications

Donnan dialysis has been developed into a useful tool for sample pretreatment and enrichment. As a result trace analysis for anions and cations in water has been simplified.

The procedures should find wide application. For example, we have used Donnan dialysis in a study on the Cedar Creek Reservoir, Jackson County, Illinois. Dialysis of grab samples improved their stability in storage, permitted differentiation between ionic and

molecular mercury, and provided a means of detecting lead at the sub-ppb level. Donnan dialysis has also been used to eliminate matrix effects on the determination of anions in a coal ash sluice pond.

Attempts to use Donnan dialysis coupled to electrochemical deactivation as a continuous ion removal system had limited success. Electrodialysis proved to be a more rapid means of transferring the ions from the sample into a receiver electrolyte and also has the advantage of de-salting a sample rather than exchanging ions. Nevertheless, Donnan dialysis was not so slow as to be completely discounted for future use. In cases where large membrane areas are more practical (or more convenient) than high applied currents, Donnan dialysis would be useful; in addition, it must be recognized that this technique replaces sample ions with relatively innocuous ones from the receiver electrolyte rather than deionizing the sample. A possible application is the softening of water.

The electrochemical stage of the removal system was successfully developed for the case of nitrate. A practical means of reducing nitrate to ammonia was developed. A method for plating out phosphate was not successful. A combination of Donnan dialysis and

electrochemical reduction may be useful for removing nitrate from small water wells.

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